

PROPERTIES OF CEMENT-FLY ASH MIXTURES WITH SUBSTANDARD FLY ASH AS A PARTIAL CEMENT AND FINE AGGREGATE REPLACEMENT

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Abstract

This research investigated the effects of using a substandard fly ash as a partial cement and/or fine aggregate replacement on the basic and durability properties of cement-fly mixtures. Experimental results showed that utilizing the substandard fly ash led to increase in water requirement and autoclave expansion of pastes. The strength activity indexes of the substandard fly ash passed the requirements of TIS 2135 and ASTM C618. Utilization of the substandard fly ash as cement replacement led to higher expansion of mortar bars stored in water and sodium sulfate expansion as compared to that of the OPC mixture. However, sodium sulfate resistance of mortar mixtures improved when utilizing the substandard fly ash as sand replacement material. The compressive strength of concrete at all ages was higher with the increase of the content of the substandard fly ash as sand replacement material. When the substandard fly ash was used as cement replacement material in concrete, the carbonation depth increased. On the other hand, the use of the substandard fly ash as sand replacement material decreased the carbonation depth of the concrete. Utilization of the substandard fly ash, both to replace cement and/or fine aggregate, reduced the rapid chloride penetration of the concrete.

Keywords: Compressive strength, Durability, Expansion, Fine aggregate, Fly ash, Sand

Introduction

Concrete consumption worldwide has been immensely increased due to rapid urbanization that leads to enormous demand of aggregates. The consumption of aggregates is estimated at 30 billion tons annually [1]. In 2017, the estimated use of sand and gravel in construction was more than 40 billion tons [2]. Excessive mining leads to many environmental problems, such as causing floods, causing erosion and changing the ecosystem of the rivers. There has been evidence of sand scarcity in many countries in the ASEAN region, such as Thailand, Singapore, Vietnam, and Indonesia [2-4]. Moreover, the escalated sand price is also a major challenge to the construction industry [5,6].

In another aspect, there are many fly ashes that cannot be used in any applications. Many countries around the world have difficulties in utilizing fly ash. In China, approximately 200 million tons of fly ash has to be stored up every year because it cannot be utilized [7]. From 2017 to 2018, India used only 67% of its fly ash, which led to 65 million tons of unutilized fly ash [8]. In the US, approximately only 64% of the coal ash generated

in 2017 was utilized [9]. These data validate the huge amount of unutilized fly ashes that are not used in any applications. There are many health and environmental problems caused by the disposal of fly ash. Disposing the fly ash into the water source (ponds, rivers, seas, etc.) pollutes the water. Moreover, the disposal of fly ash demands a huge area of landfills. The disposing of fly ash to the landfills can lead to the leaching process, which contaminates the groundwater [10].

Since there are large amount of unutilized fly ashes worldwide, there have been many studies to find possible ways to utilize them. Among these studies, there are researches that study the utilization of low-quality fly ashes or substandard fly ashes as cement replacement materials. Demis et al. [11] studied the effectiveness of using different biomass ashes as cement replacement materials in concrete. The study concluded that biomass ashes such as rice husk ash, palm oil fuel ash, and wood ash could be used in concrete up to 20%. A study by Chatchawan [12] on the use of fly ash containing high free lime and high SO₃ contents stated that utilizing high free lime and high SO₃ fly ash to replace 30% of cement in expansive concrete could reduce the expansive additive dosage by approximately 22 kg/m³. Phethany et al. [13] studied the use of high LOI fly ash in concrete and stated that the compressive strength of concrete gradually increased when the LOI content of the fly ash increased from 0.77% to 12.37%. The compressive strength of concrete started to decrease when the LOI content in fly ash exceeded 12%. Recently, fly ash from a power plant in Thailand, which does not conform to the standards for utilization in concrete, was found. This research aims to provide information on the properties of cement-fly ash mixtures containing the substandard fly ash to enable correct judgement whether to use or not use this substandard fly ash. Moreover, this study aims to provide the attentions to be considered when using the substandard fly ash to prevent misuse of this fly ash as well as to provide cautions on adverse effects caused by the use of the substandard fly ash and its limitation.

Experimental Programs

Materials

The properties of mixtures containing OPC type I and the substandard fly ash were studied. The OPC type I following ASTM C150 [14] and TIS 15 [15] standards was used in this study. The substandard fly ash was obtained from a power plant in Rayong Province, eastern part of Thailand. For tests on pastes, the substandard fly ash was used as a cement replacement material. The substandard fly ash was used in the mortar tests in 2 ways; as cement replacement material and as sand replacement material. For the tests on concrete, the substandard fly ash was used to replace cement, to replace sand and to replace both cement and sand. The substandard fly ash particles are porous with irregular shapes, as illustrated in Figure 1. Chemical compositions of the substandard fly ash are given in Table 1. The substandard fly ash incorporates low content of SiO₂ (18.75%), which is lower than the minimum requirement in the TIS 2135 standard (30%) [16]. The substandard fly ash also incorporates a high percentage of SO₃ (9.01%), which is higher than the maximum requirement of TIS 2135 [16] and ASTM C618 [17] standards (5.0%). Physical properties of the OPC and the substandard fly ash are illustrated in Table 2. The substandard fly ash has a specific gravity of 2.67, and Blaine fineness of 2237 cm²/g. Table 3 shows the physical properties of the aggregates used in this study. River sand and limestone were used as fine and coarse aggregates, respectively. A naphthalene-based superplasticizer named “Kao-Mighty MX-T” was used at different dosages to obtain the initial slump of the tested concrete within 12±2.5cm. This superplasticizer complies with Type F according to ASTM C494 standard [18].

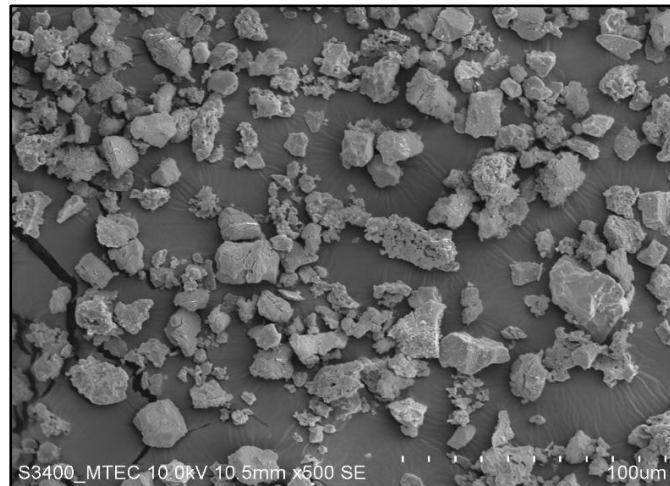


Figure 1. Scanning electron microscope (SEM) image of the substandard fly ash

Table 1. Chemical Compositions of the Binders

Chemical Composition (%)	OPC Type I	Fly Ash
SiO ₂	18.93	18.75
Al ₂ O ₃	5.51	9.59
Fe ₂ O ₃	3.31	5.22
CaO	65.53	46.88
MgO	1.24	1.86
Na ₂ O	0.15	1.25
K ₂ O	0.31	0.76
SO ₃	2.88	9.01
LOI	-	7.36
Free lime	0.75	29.44

Table 2. Physical Properties of the Binders

Physical Property	OPC Type I	Fly Ash
Specific gravity	3.15	2.67
Blaine fineness (cm ² /g)	3054	2237

Table 3. Physical Properties of the Aggregates

Physical Property	Fine Aggregate	Coarse Aggregate
Specific gravity	2.54	2.78
Absorption (%)	1.21	0.40

Mix Proportions

The properties of pastes, mortars, and concrete were studied. Several experiments, such as autoclave expansion, water requirement, expansion of mortar bars stored in water, Na₂SO₄ expansion, compressive strength, carbonation depth, and RCPT tests, were conducted. The experimental programs of cement-fly ash mixtures are illustrated in Table 4.

There were two replacement methods (cement replacement and sand replacement) in the cases of mortar and concrete tests. For the cement replacement, the replacement percentage was based on the original cement weight. For sand replacement, the amount of fly ash was also determined by the original cement weight. After that, the same sand volume as that of the fly ash was excluded from the mixture. It is noted that the replacement percentages in both cement replacement and sand replacement cases were calculated based on the original cement weight due to the reason that the results from these two cases were compared to evaluate the effectiveness of each replacement method. In addition, the fly ash replacing sand also plays the role of binder in the concrete. The replacement methods used in this study were similar to those used in the studies of, Hung [19], Papadakis [20], Siddique [21] and Surangi et al. [22].

There were six mixtures of the concrete tested in this study. For all mixtures, w/b of 0.60 with the same paste content was used. The control mix (FC0FS0) was the cement-only concrete. There were two mixtures with only sand replacement by the substandard fly ash. These mixtures were FC0FS20 and FC0FS40, with sand replacement percentages of 20% and 40%, respectively. The other three mixtures contain the substandard fly ash as combined cement replacement and sand replacement. These three mixtures were the mixtures with 15% cement replacement by the substandard fly ash and sand replacement by the substandard fly ash with the replacement percentages of 0% (FC15FS0), 20% (FC15FS20), and 40% (FC15FS40). The concrete mix proportions of this study are illustrated in Table 5.

Test Methods

Autoclave Expansion of Pastes

Autoclave expansion of pastes was conducted to investigate the expansion induced mainly by the hydration of MgO and CaO. The test procedure is based on the ASTM C151 standard [23]. The specimens used in the experiment were 25x25x285 mm prisms.

Table 4. Experimental Program of Pastes, Mortars and Concrete

Test Items	Type	R _c (%)	R _s (%)	w/b
Autoclave expansion	Paste	0, 20, 30, 40, 50	-	NM
Water requirement	Mortar	0, 20, 30, 40, 50	0, 20, 30, 40, 50	WR
Strength activity index	Mortar	0, 20	-	WR
Expansion of mortar bars stored in water	Mortar	0, 20, 30, 40, 50	0, 20, 30, 40, 50	WR
Sodium sulfate expansion	Mortar	0, 20, 40	0, 20, 40	0.55
Compressive strength	Concrete	0, 15	0, 20, 40	0.60
Carbonation depth	Concrete	0, 15	0, 20, 40	0.60
RCPT	Concrete	0, 15	0, 20, 40	0.60

Note: R_c (%) is the percentage of cement replaced by fly ash (by weight of original cement), R_s (%) is the percentage of sand replaced by fly ash (by weight of original cement), w/b is design water to binder ratio, NM is water content of paste to obtain the penetration of 10±1mm by the plunger of Vicat apparatus (w/b at normal consistency), WR is water content of mortar to obtain the slump flow of 110±5mm after impact 25 times in 15 seconds using flow table apparatus.

Table 5. Concrete Mix Proportions of the Study

Design Parameters					Unit Content (kg/m ³)						
Mix ID	w/b	R _c (%)	R _s (%)	R _{s(eq)} (%)	Cement	FAC	FAs	Water	Sand	Gravel	Admixture
FC0FS0	0.6	0	0	0	282	0	0	167	830	1139	2.8
FC0FS20	0.6	0	20	6.8	282	0	56	167	776	1139	3.7
FC0FS40	0.6	0	40	13.6	282	0	113	166	722	1139	5.1
FC15FS0	0.6	15	0	0	237	42	0	165	830	1139	3.6
FC15FS20	0.6	15	20	6.7	237	42	56	165	777	1139	4.7
FC15FS40	0.6	15	40	13.4	237	42	112	163	723	1139	6.6

Note: w/b is design water to binder ratio, R_c(%) is the percentage of cement replaced by fly ash (by weight of original cement), R_s(%) is the percentage of sand replaced by fly ash (by weight of original cement), R_{s(eq)}(%) is the percentage of sand replaced by fly ash (by weight of total fine aggregate), FAC is the weight of fly ash to replace cement, FAs is the weight of fly ash to replace sand.

The w/b used in the experiment was the w/b at the normal consistency. For autoclave expansion tests, the substandard fly ash was used as cement replacement at 20%, 30%, 40%, and 50%.

Water Requirement of Mortars

This test was conducted to determine the w/b to obtain the slump flow of 110±5mm after the flow table impact of 25 times in 15 seconds. The w/b obtained from the water requirement test was used for the tests of the strength activity index and expansion of mortar bars stored in water. The test procedure of water requirement followed the ASTM C1437 standard [24]. For this test, the substandard fly ash was used as cement replacement at 20%, 30%, 40%, and 50%. Similarly, the substandard fly ash was also used as sand replacement at 20%, 30%, 40%, and 50%.

Strength Activity Index

The test procedure was based on ASTM C311 [25]. Strength activity index is an index to represent the reactivity of a particular fly ash and it is used to justify the quality of the fly ash compared to the requirement set by the standard as well as is used to compare reactivity of different fly ash. Therefore, the replacement percentage is fixed at 20% by ASTM C311 as a standard replacement for testing the index. The specimens used in this test were 50x50x50mm cubes. The w/b used in this experiment was equal to the w/b at the water requirement. There were 2 mixtures for the strength activity index test. These two mixtures were the OPC mixture and the mixture containing the substandard fly ash as cement replacement material at 20%.

Expansion of Mortar Bars Stored in Water

This experiment was conducted to investigate the expansion of mortars due to sulfur trioxide (SO₃) in the binders. The expansion may become excessive when the sulfate content in the binder is too high. The test procedures followed the ASTM C1038 standard [26]. The

specimens used in the experiment were 25x25x285mm prisms. The w/b used in this experiment was the same as that obtained from the water requirement test. For the expansion of mortar bars stored in water tests, the tested mixtures were the same as those of the water requirement tests.

Sodium Sulfate Expansion of Mortars

The sodium sulfate expansion of mortars was conducted to examine the mortar ability to resist the expansion caused by sodium sulfate ions. For this test, 25x25x285mm prism specimens were used. The w/b used in this test was 0.55, with sand to binder ratio of 2.75 for all tested mixtures. The specimens were cast and demolded 24 hours after casting. Subsequently, the specimens were water-cured for 28 days. Then, the specimens were measured for the initial length and then immersed in the Na₂SO₄ solution. The solution was made from mixing 50g of Na₂SO₄ with water to obtain 1 liter of solution. The substandard fly ash was used to replace cement at 20% and 40%. Similarly, the substandard fly ash was also used to replace sand at 20% and 40%. Additionally, the substandard fly ash was used as combined cement replacement material and sand replacement material in two mixtures with the cement replacement percentage of 20% and the sand replacement percentages of 20% and 40%.

Compressive Strength of Concrete

This test was conducted by following the EN 12390-3 standard [27]. The specimens of the compressive strength test were 100x100x100mm cubes. Instantly after casting, the specimens were covered by plastic sheets and aluminum foils to prevent water evaporation from the specimens. Subsequently, the specimens were demolded after 24 hours and wrapped by three layers of aluminum foils and three plastic sheet layers. The seal-cured specimens were used to conduct the tests at 1, 3, 7, 28, and 91 days.

Carbonation Depth of Concrete

This experiment was conducted to investigate the penetration of CO₂ into the concrete. The test procedures followed the RILEM recommendation CPC-18 [28]. The specimens used in this test were 100x100x100mm cubes. The specimens were seal-cured for 28 days. After that, the specimens were stored in a carbonation chamber with a CO₂ concentration of 4%, temperature of 40±1^oC and relative humidity of 50±5%. The specimens were stored until reaching the exposure periods of 28 and 91 days. A solution of 1% phenolphthalein in 70% ethyl alcohol was sprayed on the broken concrete surface. The concrete surface area that remained colorless after the spraying was considered as the carbonated area. The non-carbonated area changed its color to purple. The carbonation depth was calculated from twelve measurements per a concrete specimen, by measuring carbonation depth on three different locations of each side of the broken concrete surface. The carbonation depth of three different specimens from the same mix proportion were used to determine the mean carbonation depth.

Rapid Chloride Penetration of Concrete

The RCPT test was conducted to rapidly investigate the concrete resistance to chloride ion ingress. The test procedures followed the ASTM C1202 standard [29]. The specimens used in the experiment were cylinders having 50mm in height and 100mm in diameter. The specimens were seal-cured until reaching the test ages. The test ages of the rapid chloride penetration test were 28 and 91 days. The amount of charge passed in 6 hours through the 50x100mm specimens was measured.

Results and Discussions

Autoclave Expansion of Pastes

Figure 2 shows the results of the autoclave expansion test. All tested mixtures containing the substandard fly ash exhibited higher autoclave expansion than the OPC mixture. The autoclave expansions of pastes containing the substandard fly ash were 0.013%, 0.020%, 0.032% and 0.037% for the cement replacement percentages of 20%, 30%, 40% and 50%, respectively. The autoclave expansion of paste containing the substandard fly ash increased with higher replacement percentage due to the high contents of CaO (46.88%) and free lime (29.44%) in the substandard fly ash. It was reported in a previous study that higher free lime content in the substandard fly ash led to higher autoclave expansion of pastes [30].

ASTM C618 [17] limits the autoclave expansion of a paste at lower than 0.80%. The pastes containing the substandard fly ash up to 50% still exhibited lower autoclave expansion than the allowable expansion stated in the standard.

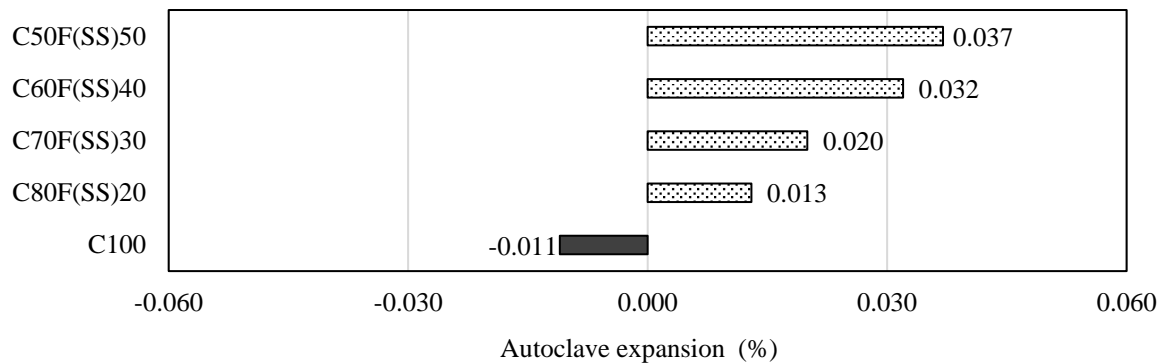


Figure 2. Autoclave expansion of pastes

Water Requirement of Mortars

Figure 3 illustrates the results of water requirement of the tested mortars. The water requirements of the mixtures containing the substandard fly ash as cement replacement were 108.6%, 112.3%, 116.3%, and 120.0% for the replacement percentages of 20%, 30%, 40%, and 50%, respectively. The water requirements of mortar mixtures increased with the higher cement replacement percentage by the substandard fly ash. Nawaz et al. [30] stated that higher free lime in fly ash was one of the reasons for the increased water requirement. Moreover, there is a correlation between LOI content in fly ash and the water requirement as reported by Feng et al. [31]. The relationship showed that fly ash with LOI content higher than 3% was likely to increase the water requirement. Thus, the higher water requirement of mortar mixtures containing the substandard fly ash is not only due to the high content of free lime (29.44%) but also high LOI content (7.36%) in the fly ash.

For the sand replacement case, the mortar mixtures containing the substandard fly ash as a sand replacement required higher water content for obtaining the 110±5% flow compared to the mixtures containing the substandard fly ash as cement replacement material. The water requirements of the mixtures containing the substandard fly ash as sand replacement material were 109.3%, 113.4%, 120.6%, and 129.9% for the sand replacement percentages of 20%, 30%, 40%, and 50%, respectively. The water requirements of mortar mixtures increased with higher sand replacement percentage by the substandard fly ash, which was mainly due to the higher actual total binder content and lower actual w/b of the mortar mixtures containing the substandard fly ash as sand replacement.

Strength Activity Index

Figure 4 shows the results of the strength activity index. At 7 days of age, the mixture containing the substandard fly ash as cement replacement material exhibited lower strength activity index than the OPC mixture. The strength activity index of the mortar with 20% cement replacement by the substandard fly ash was 96.2%.

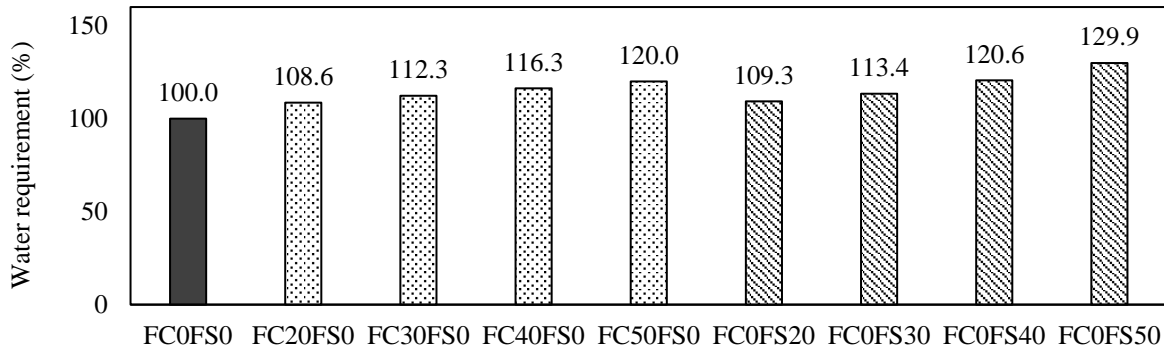


Figure 3. Water requirement of mortars

The strength activity index of 96.2% at 7 days of age passes the requirements of the ASTM C618 [17] and TIS 2135 [16] standards. At 28 days of age, the mixture containing the substandard fly ash as cement replacement material exhibited a lower strength activity index than the OPC mixture. The strength activity index of the mortar with 20% cement replacement by the substandard fly ash was 92.1%. The strength activity index of 92.1% at 28-days age also passes the requirements of the ASTM C618 [17] and TIS 2135 [16] standards. It should be noted that the strength activity index at 28 days of the mortar with the substandard fly ash was not higher but lower than the index at 7 days, indicating that the pozzolanic reaction of the substandard fly ash was not so active.

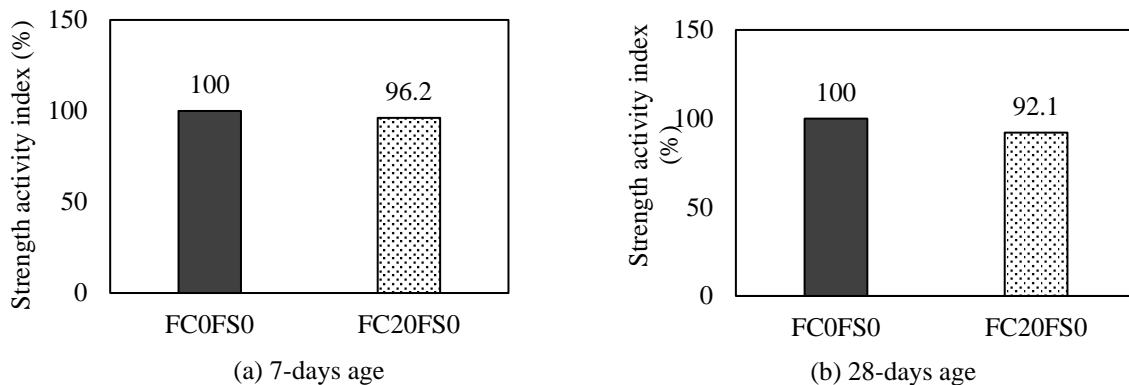


Figure 4. Strength activity index

Expansion of Mortar Bars Stored in Water

Figure 5 shows the results of the expansion of mortar bars stored in water. The expansions of mortar mixtures containing the substandard fly ash as cement replacement were 0.011%, 0.022%, 0.034% and 0.060% for the cement replacement percentages of 20%, 30%, 40% and 50%, respectively. The expansion is due to the high SO₃ content ((9.01%) in the fly ash.

For sand replacement, the mortar mixtures containing the substandard fly ash as sand replacement showed lower expansion than the mixtures containing the fly ash as cement replacement when compared at the same replacement percentage. The expansions of mortar

mixtures containing the substandard fly ash as sand replacement material were 0.007%, 0.015%, 0.023%, and 0.032% for the sand replacement percentages of 20%, 30%, 40%, and 50%, respectively. The decrease of mortar expansion when utilizing the substandard fly ash as sand replacement as compared to the mixtures containing the substandard fly ash as cement replacement is due to the lower actual w/b resulting from the higher actual total binder content.

ASTM C150 [14] limits the expansion of mortar bars stored in water to 0.02%. The utilization of the substandard fly ash as cement replacement material at the replacement percentages higher than 20% leads to higher expansion than the limitation of the standard. For the sand replacement case, using of the substandard fly ash as sand replacement material at the replacement percentages higher than 30% also leads to higher expansion than the limitation. Therefore, there is a potential that excessive expansion will occur if the substandard fly ash is used in concrete. This excessive expansion can cause damage to the concrete with the substandard fly ash.

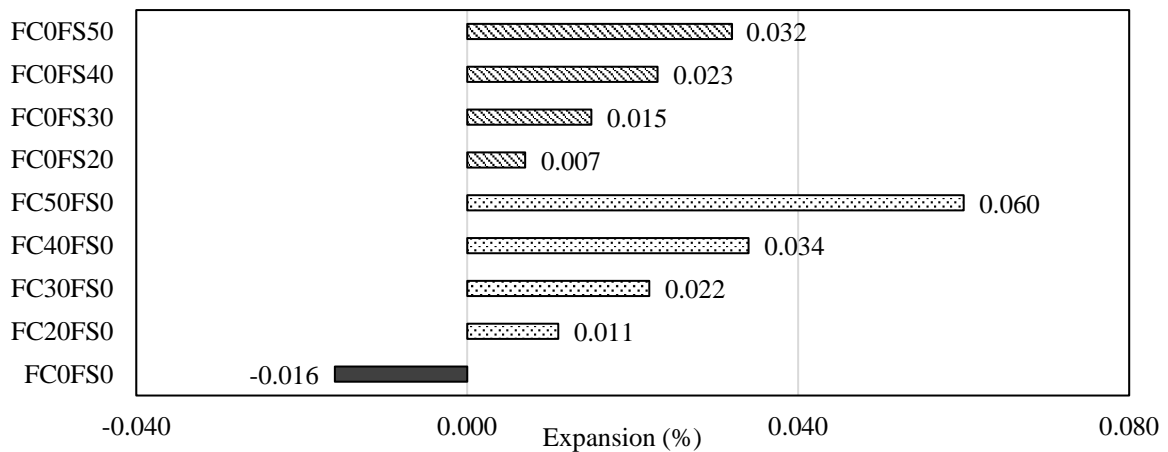


Figure 5. Expansion of mortar bars stored in water

Sodium Sulfate Expansion of Mortars

Figure 6 shows the results of the Na_2SO_4 expansion of mortar. The utilization of the substandard fly ash as cement replacement material led to higher sulfate expansion than that of the OPC mixture. The expansions of the mixtures with 20% and 40% cement replacement by the substandard fly ash were 0.159% and 0.245%, respectively. The expansion increased with the increase of the cement replacement percentage by the substandard fly ash. Nawaz et al. [30] observed that higher free lime content in the substandard fly ash led to higher Na_2SO_4 expansion of mortar mixtures. Thus, the high expansion is considered due to the high contents of free lime (29.44%) and SO_3 (9.01%) in the substandard fly ash. For the mixtures with sand replacement by the substandard fly ash at 20% and 40%, the expansions were 0.021 and 0.022, respectively. Utilization of the substandard fly ash to replace sand showed lower expansion in sodium sulfate solution than the mixtures containing the substandard fly ash as cement replacement material. It should be noted that the substandard fly ash should not be recommended for Na_2SO_4 resistance despite showing lower expansion when using as sand replacement material as it has a high potential to cause excessive expansions, as can be seen in the case when using it to replace cement.

In the case of using the substandard fly ash as combined cement replacement material and sand replacement material, the expansions were higher than that of the sand replacement-only mixtures. However, the expansions were lower than that of the cement

replacement-only mixtures. The mixture containing the substandard fly ash as cement replacement material at 20% and as sand replacement material at 20% exhibited an expansion of 0.041%. When using the substandard fly ash to replace cement at 20% and sand at 40%, the expansion was 0.050%. For the mortar mixtures containing the substandard fly ash as combined cement replacement material and sand replacement material, the sodium sulfate expansion increased with the higher sand replacement percentage.

The ASTM C618 standard [17] limits the maximum allowable sulfate expansion of cement-fly ash mortar to 0.10% for moderate sulfate exposure after 6 months of immersion. The mixtures containing the substandard fly ash as cement replacement material at 20% and 40% do not pass the requirement of the sulfate resistance of the standard. This shows that the substandard fly ash is not good for Na_2SO_4 resistance. It is generally known that fly ash normally reduces the sodium sulfate expansion due to its pozzolanic reaction and cement dilution effect, and higher fly ash content leads to lower expansion of mortars in Na_2SO_4 solution [32]. However, in the case of the substandard fly ash, higher fly ash content in the mixture leads to higher Na_2SO_4 expansion. This implies that the pozzolanic reactivity of this substandard fly ash is not effective. The increased Na_2SO_4 expansion of the mortars containing the substandard fly ash as cement replacement is due to the low pozzolanic reactivity, and the high contents of free lime and SO_3 of the substandard fly ash.

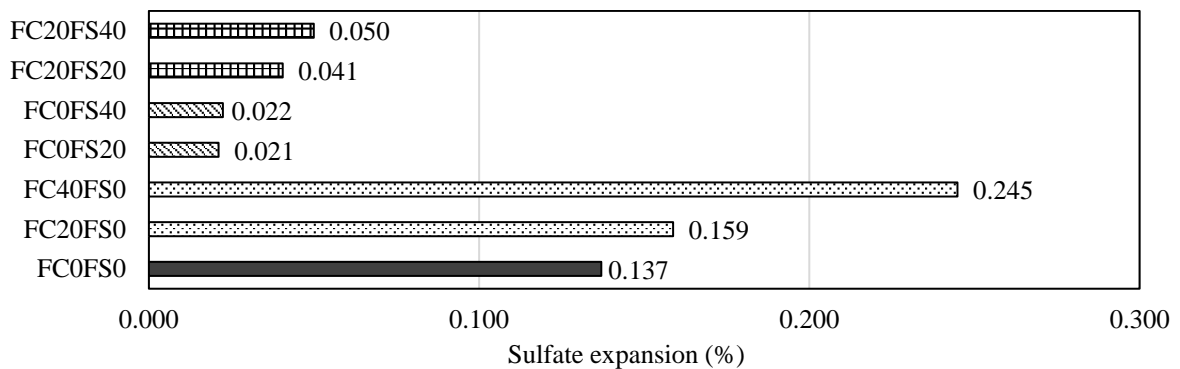


Figure 6. Na_2SO_4 expansion of mortars at the immersion age of 6 months

Compressive Strength of Concrete

Figure 7 shows the results of the compressive strength of concrete. The mixtures containing the substandard fly ash as sand replacement exhibited higher strength than the OPC mixture at all curing ages. The compressive strength increased with the increase of the sand replacement percentage. This strength improvement is due to the higher actual total binder content of the mixtures and lower actual w/b.

However, the mixture with 15% cement replacement by the substandard fly ash exhibited lower compressive strength than the OPC mixture at all tested ages. Generally, there is a strength reduction at an early age when utilizing a fly ash as cement replacement material because of the lower cement content and delayed reactions. However, the reduced strength at the early age with the presence of the substandard fly ash as a cement replacement was small due to the high contents of CaO and free lime in the fly ash, which produced extra $\text{Ca}(\text{OH})_2$ needed for the pozzolanic reaction [33,34]. Meanwhile, there is no significant strength improvement at the age of 91 days when utilizing the substandard fly ash as a cement replacement because of the low content of SiO_2 in the fly ash. Silica (SiO_2) is an important chemical for the pozzolanic reaction, which is the dominant reaction contributing to the later age of concrete.

At the early ages, the mixture with combined 15% cement replacement and 20% sand replacement exhibited similar compressive strength as compared to the OPC mixture. However, there was an improvement of the compressive strength of this mixture at the later ages due to the higher actual total binder content and lower actual w/b of the mixture compared to those of the OPC mixture. For the mixture with combined 15% cement replacement and 40% sand replacement, the compressive strength was higher than the OPC mixture at all ages.

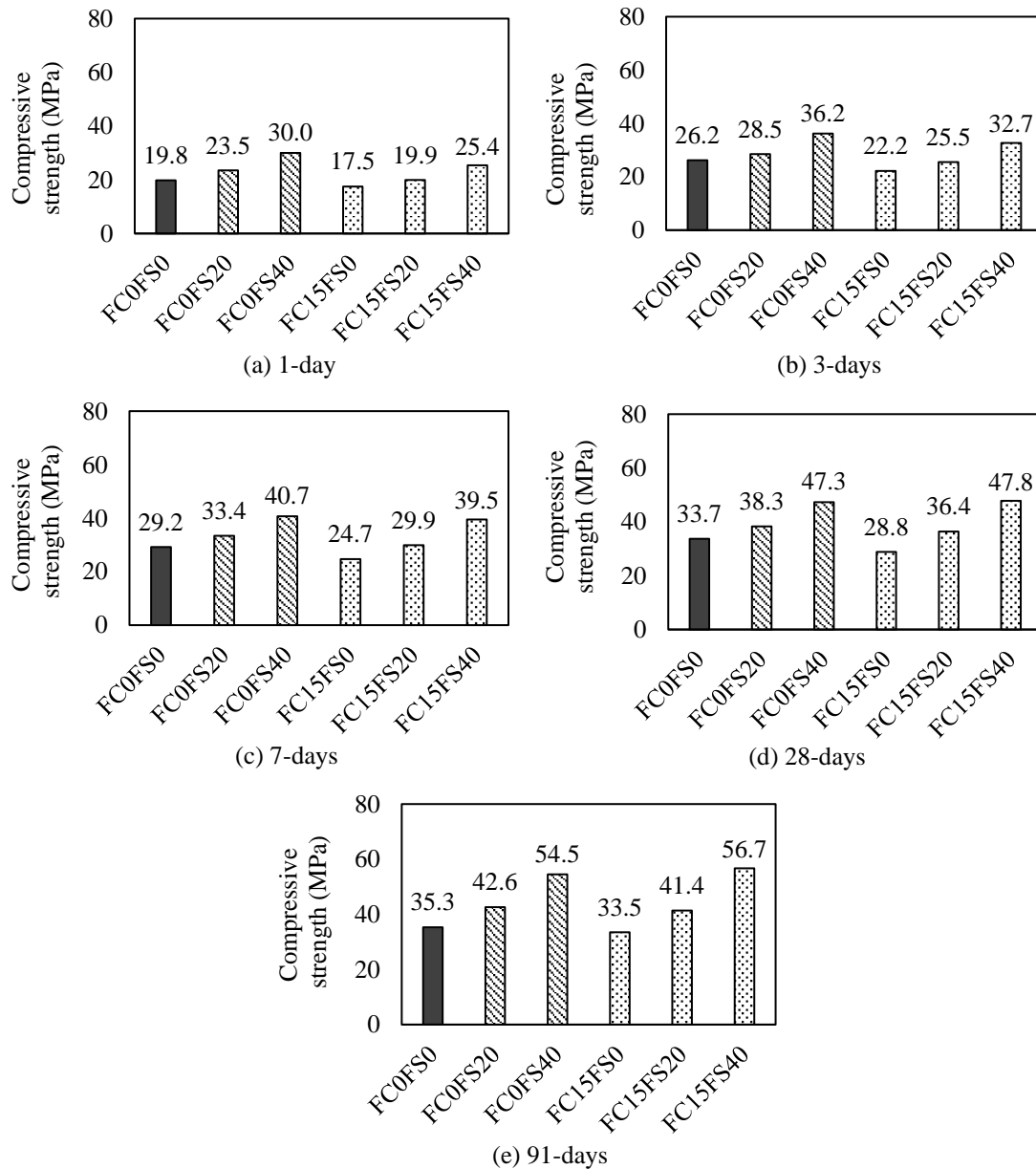


Figure 7. Compressive strength of concrete at different curing ages

Carbonation Depth of Concrete

Figure 8 illustrates the results of carbonation depth of the tested concrete mixtures. At 28 days of exposure, the carbonation depth of the OPC mixture was 11.5mm. The mixtures with only sand replacement exhibited lower carbonation depth with the values of 9.3mm and 7.0mm for the sand replacement percentages of 20% and 40%, respectively. At 91 days of exposure, the carbonation depths of the mixtures were 18.5mm, 15.3mm, and 10.7mm for

the sand replacement percentages of 0%, 20%, and 40%, respectively. The carbonation depth decreased with the increase of the sand replacement percentage by the substandard fly ash. The carbonation depth decreased as compared to that of the OPC mixture due to the higher actual total binder content and lower actual w/b of the mixtures containing the substandard fly ash as sand replacement material. Moreover, the substandard fly ash incorporated high contents of CaO and free lime, which are known to enhance alkalinity and therefore, is more advantageous for the carbonation resistance of concrete when compared to low CaO and low free lime fly ashes. The CaO compounds and free lime react with water in the system to form extra $\text{Ca}(\text{OH})_2$, which is known to delay the carbonation ingress into the concrete. It was previously found that utilizing high-calcium fly ash in mortar led to better resistance to carbonation than that of the low-calcium fly ash mortar [35,36]. Hence, the improvement of the carbonation resistance of the concrete mixtures containing the substandard fly ash as sand replacement material was due to the higher actual total binder content and lower actual w/b of the concrete mixtures as well as the high contents of CaO (46.88%) and free lime (29.44%) in the fly ash.

For the 15% cement replacement mixture, the carbonation depths were 15.5mm and 23.4mm at the exposure ages of 28 and 91 days, respectively. For the concrete mixture with combined 15% cement replacement and 20% sand replacement, the carbonation depths were similar to those of the OPC mixture with the values of 11.9mm and 18.2mm at the exposure ages of 28 and 91 days, respectively. However, the concrete mixture with combined 15% cement replacement and 40% sand replacement showed lower carbonation depths than those of the OPC mixture with the values of 7.7mm and 12.5mm at the exposure ages of 28 and 91 days, respectively, mainly due to lower actual w/b. When using the substandard fly ash as a cement replacement material, the carbonation depth increased due to the reduced alkalinity of the concrete matrix, mainly by cement dilution effect.

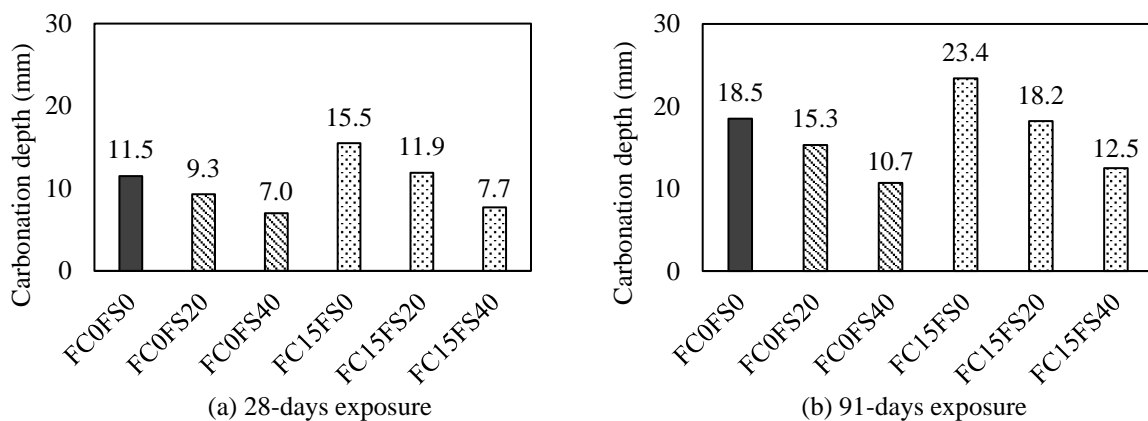


Figure 8. Carbonation depth of concrete at different exposure ages

Rapid Chloride Penetration of Concrete

Figure 9 illustrates the results of the charge passed of the tested concrete mixtures. When tested after 28 days of curing, the charge passed of the OPC mixture was 6616C. The mixtures with only sand replacement exhibited lower charge passed with the values of 4924C and 2759C for the sand replacement percentages of 20% and 40%, respectively. At 91 days of age, the OPC mixture exhibited the charge passed of 4483C. At the same age, the values of charge passed of the mixtures containing the substandard fly ash as a sand replacement were 3103C and 1483C for the sand replacement percentages of 20% and 40%, respectively. The charge passed of the concrete was lower with the increase of the sand replacement

percentage due to higher actual total binder content and lower actual w/b, which led to the reduction of porosity in the concrete. The better resistance to chloride ions penetration of the mixtures with sand replacement by the substandard fly ash is consistent with the findings of Papadakis [35] and Surangi et al. [22].

In the case of 15% cement replacement, concrete mixtures exhibited the charge passed of 5299C at 28 days of curing. For the mixtures with combined cement replacement and sand replacement by the substandard fly ash, the charge passed through the specimens were 4114C and 2536C for the sand replacement percentages of 20% and 40%, respectively. At 91 days of curing, the mixture with 15% cement replacement by the substandard fly ash showed the charge passed of 3833C. At the same age, the mixtures with combined 15% cement replacement and sand replacement by the substandard fly ash show the charge passed of 2446C and 1338C for the sand replacement percentages of 20% and 40%, respectively.

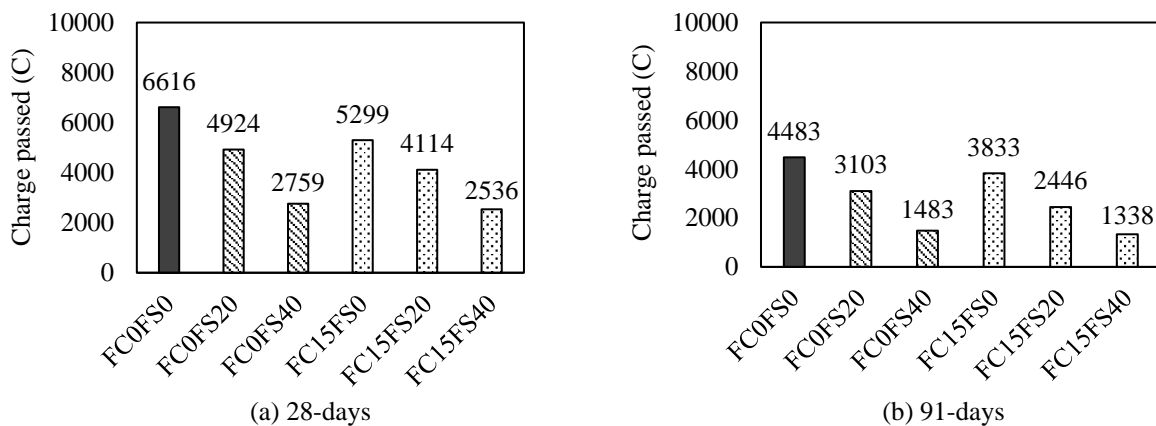


Figure 9. Charge passed of concrete at different curing ages

Overall Performance Evaluation

Table 6 compares the performances of the properties of the mixtures containing the substandard fly ash as cement replacement or as sand replacement to those of the OPC mixture. All tested properties except the rapid chloride penetration of the mixtures containing the substandard fly ash as cement replacement are worse than those of the OPC mixture. The poor performances of the mixtures with cement replacement in the sodium sulfate expansion, and the compressive strength tests justify the low pozzolanic reactivity of the substandard fly ash. Moreover, there is an excessive expansion when using the substandard fly ash as cement replacement, which can cause damage to the cement-fly ash mixture, as discussed in the part of expansion of mortar bars stored in water results. There is also evidence of the excessive expansion of the mortars due to sodium sulfate attack. Hence, the substandard fly ash is not recommended to be used as cement replacement material due to its low pozzolanic reactivity and vulnerability to expansions.

The use of the substandard fly ash as sand replacement leads to worse performances in the aspects of water requirement and expansion of mortar bars stored in water tests than those of the OPC mixture. The performances of the other properties, such as sodium sulfate expansion, compressive strength, carbonation depth, and rapid chloride penetration of the mixtures with sand replacement, are better than those of the OPC mixture. It should be noted that the substandard fly ash should not be recommended for the purpose of Na_2SO_4 resistance despite showing lower expansion as it has high potential to cause excessive expansions, as can be seen in the case when using it to replace cement. The

substandard fly ash should not be used to replace sand at the replacement percentages higher than 30% of original cement weight since it leads to higher expansion than the limitation of the ASTM C150 standard. Figure 10 illustrates the maximum replacement percentages of the mortars to pass the requirement of the expansion of mortar bars stored in water and Na₂SO₄ expansion allowed by the standards. Figure 11 shows the equivalent sand replacement percentage by weight of total fine aggregate ($R_{s(eq)}$ (%)) to the sand replacement percentage by weight of original cement (R_s (%)). For example, the allowable sand replacement percentage of the substandard fly ash of 30% of the original cement weight is equivalent to 10.9% of the total fine aggregate weight.

Considering overall properties, the substandard fly ash is not recommended to be used as cement replacement, and it should not be used as sand replacement at the replacement percentages higher than 30% of original cement weight or approximately 10% of total fine aggregate weight. However, for better judgement in the use of the substandard fly ash in concrete, more durability properties of cement-fly ash mixtures should be studied.

Table 6. Performances of the Mixtures Containing the Substandard Fly Ash Compared to Those of the OPC Mixture

Property	Type	Cement Replacement		Sand Replacement	
		Better	Worse	Better	Worse
Autoclave expansion	Paste		o	-	
Water requirement	Mortar		o		o
Strength activity index	Mortar		o	-	
Expansion of mortar bar stored in water	Mortar		o		o
Sodium sulfate expansion	Mortar		o	o	
Compressive strength	Concrete		o	o	
Carbonation depth	Concrete		o	o	
Rapid chloride penetration	Concrete	o		o	

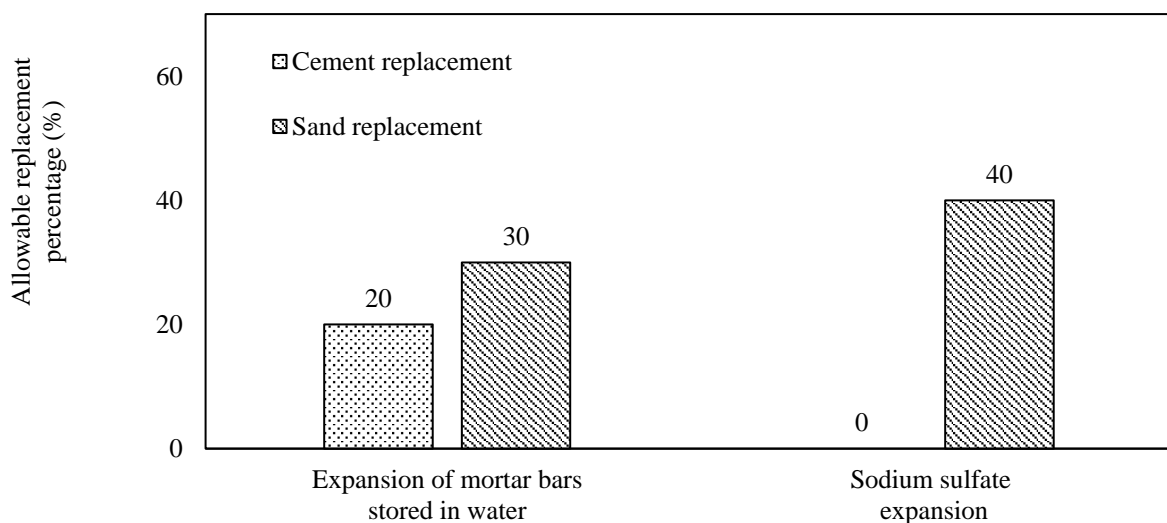


Figure 10. Allowable replacement percentages (%)

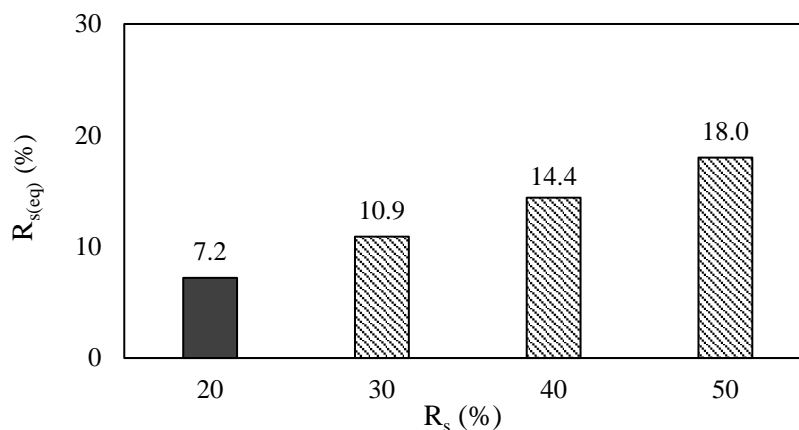


Figure 11. Conversion of the sand replacement percentage by weight of original cement (R_s (%)) to the sand replacement percentage by weight of total fine aggregate ($R_{s(eq)}$ (%)).

Conclusions

Based on the test results in this study, the following conclusions can be drawn:

1. As a cement replacement material, the substandard fly ash increases autoclave expansion of the pastes. However, replacement of the substandard fly ash up to 50% still exhibits lower autoclave expansion than the limitation of the ASTM C618 standard. The substandard fly ash increases water requirement of the mortars. Strength activity indexes of the substandard fly ash pass the requirements of the ASTM C618 and TIS 2135 standards. The expansions of mortar bars stored in water increase when the substandard fly ash is used. The use of the substandard fly ash at the cement replacement percentages higher than 20% leads to higher expansion of mortar bars stored in water than the limitation set by the ASTM C150 standard. The use of the substandard fly ash as cement replacement at 20% and 40% leads to higher Na_2SO_4 expansion than the limitation of the ASTM C618.
2. As a sand replacement material, the substandard fly ash leads to worse performances in the aspects of water requirement and expansion of mortar bars stored in water than the OPC mixture. The performances of the other properties, such as sodium sulfate expansion, compressive strength, carbonation depth, and rapid chloride penetration of the mixtures with sand replacement, are better than those of the control OPC mixture.
3. Expansion of mortar bars stored in water and sodium sulfate expansion are the most critical properties which influence the limit of replacement percentage of substandard fly ash.
4. Considering overall properties, the substandard fly ash is not recommended to be used as cement replacement, and the substandard fly ash should not be used as sand replacement at the replacement percentages higher than 10% of total fine aggregate by weight since it leads to higher expansion than the limitation set by ASTM C150 standard. However, for better understanding and judgement on the use of the substandard fly ash in concrete, more durability properties should be studied.

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